CHEMISTRY AND TRANSPORT PROPERTIES

FOR JET FUEL COMBUSTION

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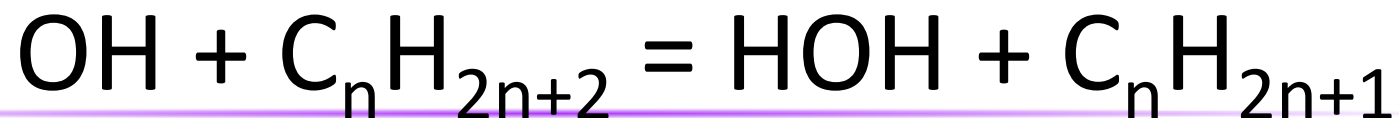NANOSCIENCE LABORATORY

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Kinetics for Jet Fuel Surrogates

- H abstraction Reaction for n-alkanes and cycloalkanes
  - Reaction Class approach to calculate rates

- The RC-TST
  - supports the assignment of equal rates for reaction in the same class through the use of the Evans/Polanyi relationship and RC-TST parameters
  - Helps to define uncertainties in the mechanism

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Reaction Class Transition State Theory

- RC-TST: reactions in a given class – same reactive moiety – have similar potential energy surfaces along the reaction coordinate.

- LER: Within a class there is a linear relationship between barrier heights and reaction energies.

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9/30/09

$OH + C_nH_{2n+2} = HOH + C_nH_{2n+1}$

- Primary Carbon
  - OH + CH3CH3 = H2O + **C**H2CH3

- Secondary Carbon
  - OH + CH3CH2CH3 = H2O + CH3**C**HCH3

- Tertiary Carbon
  - OH + (CH3)2CHCH3=H2O + (CH3)3**C**

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Reaction Class Transition State Theory

$$k_a(T) = f_\kappa(T) f_\sigma(T) f_Q(T) f_V(T) k_p(T)$$

$k_p(T)$ (Reference Reaction)

$f_\kappa(T)$ (Tunneling Factor) $= \dfrac{\kappa_a}{\kappa_p}$

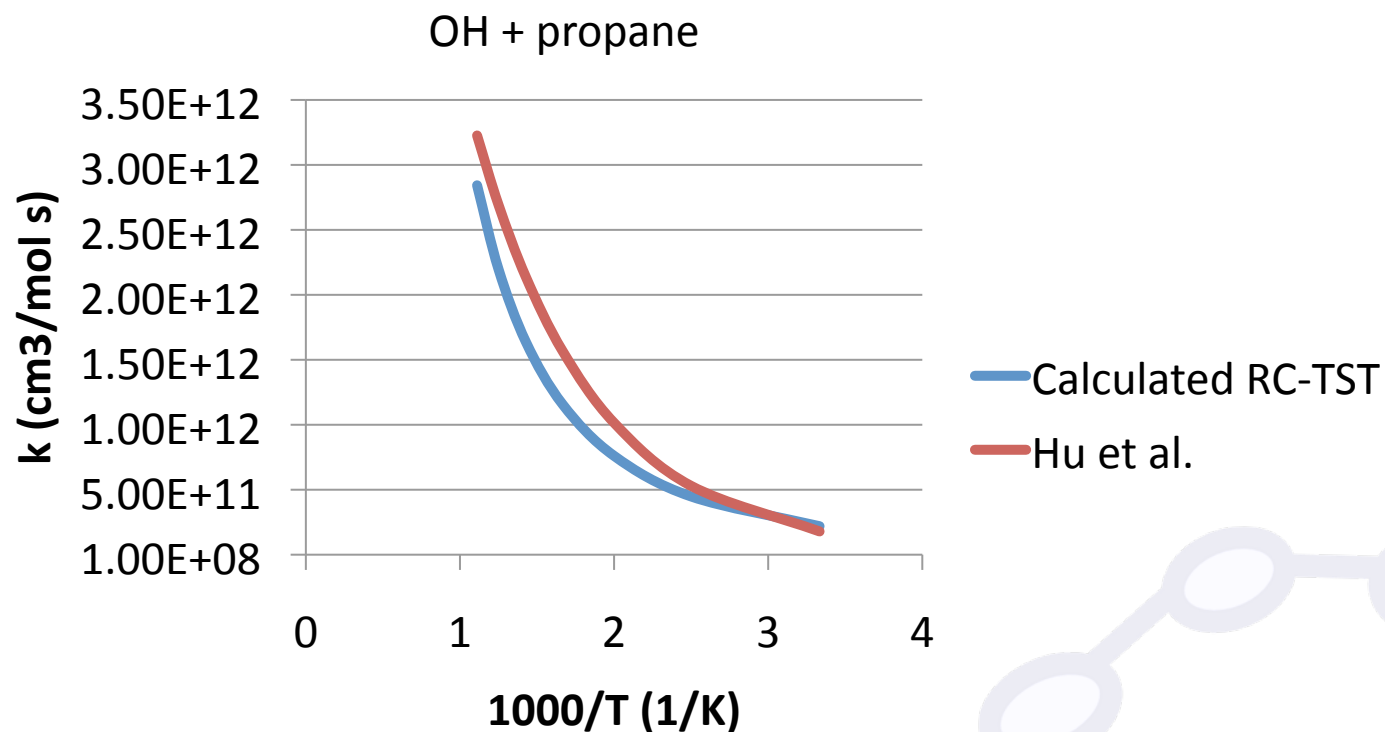$f_\sigma(T)$ (Symmetry Number Factor) $= \dfrac{\sigma_a}{\sigma_p}$

$f_Q(T)$ (Partition Function Factor) $= \dfrac{\dfrac{Q_a^\ddagger(T)}{Q_p^\ddagger(T)}}{\dfrac{\Phi_a^\ddagger(T)}{\Phi_p^\ddagger(T)}}$

$f_V(T)$ (Potential Energy Factor) $= \exp\left(-\dfrac{\Delta V_p^\ddagger - \Delta V_a^\ddagger}{R_u T}\right)$

$\Delta V^\ddagger$: Barrier Height

Truong et al. 2006

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Comparison to Known Rates

OH + propane

W. P. Hu, I. Rossi, J. C. Corchado and D. G. Truhlar, "Molecular modeling of combustion kinetics. The abstraction of primary and secondary hydrogens by hydroxyl radical," *J Phys Chem A,* vol. 101, pp. 6911-6921, 1997.

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Transport Properties

- Modeling practical fluid systems requires the knowledge of mass diffusion coefficients over wide range of temperatures and pressures.

- The strong coupling of heat conduction and molecular diffusion in reacting flows demands an accurate description of the mass diffusivities of various species for flame structure simulations.

> Small variation of fuel diffusivity should be considered to explain flame characteristics accurately

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Critical role of mass diffusivity in Combustion

Ignition characteristics of n-heptane diffusion flame

Andac and Egolfopoulos, 31th Int. Sym. Combust. 2007

- 10% perturbation of n-C7H16 diffusivity

 → 50K change of ignition temperature – influence rates

Extinction characteristics of methane/air flame

Dong et al.. 2005

- Use different transport models

  → 20 ~ 40% discrepancies in flame properties

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Critical role of mass diffusivity in Combustion

Logarithmic Sensitivity to extinction strain rate
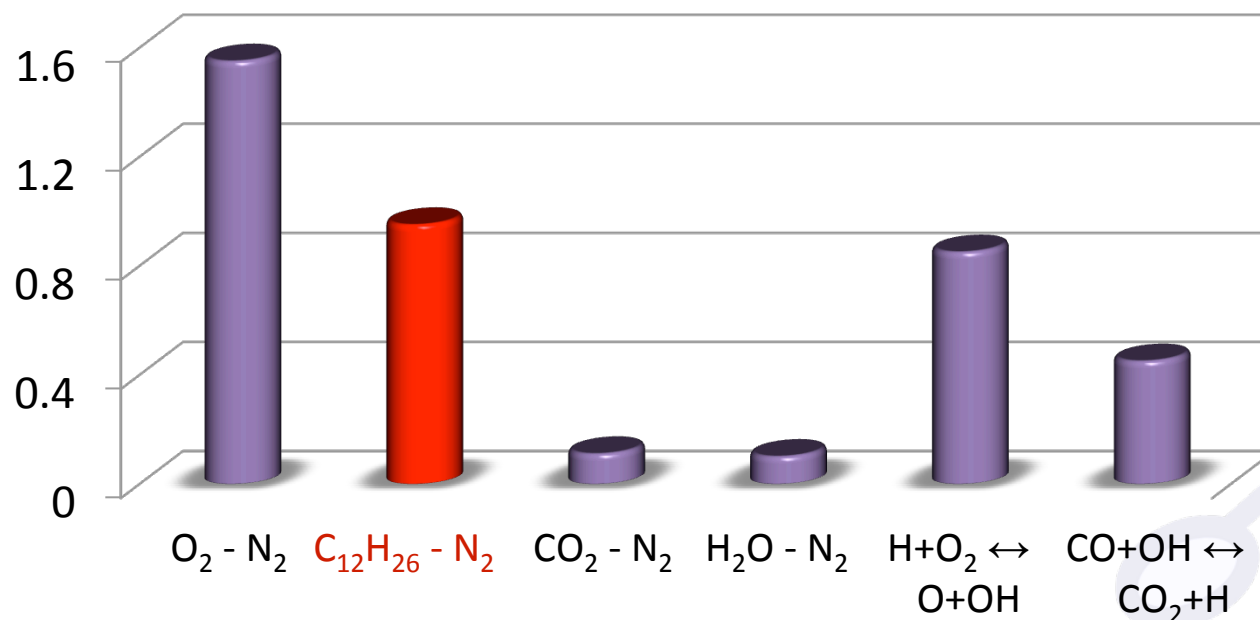
Air-$C_{12}H_{26}$

Diffusion flame

403K, 1 atm

Fuel/N_2 mass

ratio = 0.05 ~ 1

[Holley, You, Dames, Wang, Egolfopoulos, 32th Int. Sym. Combust., 2008]

non-premixed counterflow flames: Amount of fuel accessible is diffusion controlled

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Limitations/Assumptions of this approach

- Diffusion function of tabulated collision integrals, mainly derived from viscosity measurements

- Binary collision – dilute systems

- Spherical potential – averaged over orientations of the molecules

- Potential parameters

- High temperature conditions – uncertainties especially in the repulsive part of the potential

$V(r)$

σ ε

r
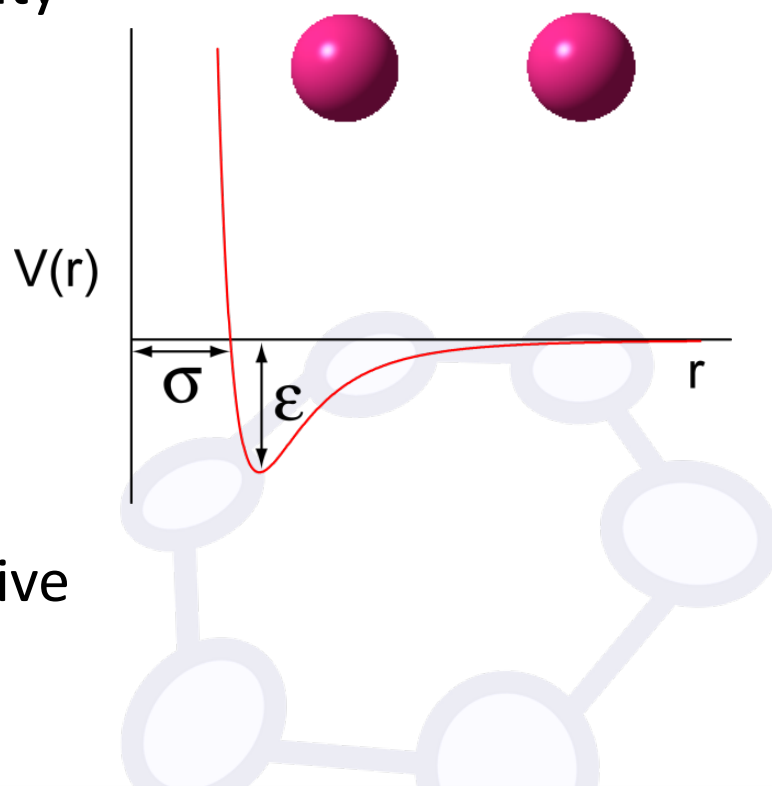
Spherical potential

❑ How good is this approach for molecules that have non-spherical

structure

$C_{16}H_{34}$

C_2H_6

$C_{14}H_{24}$
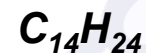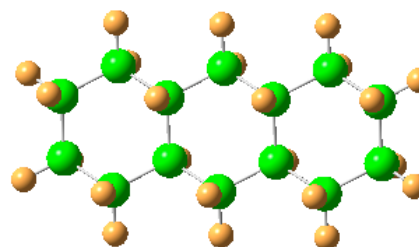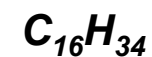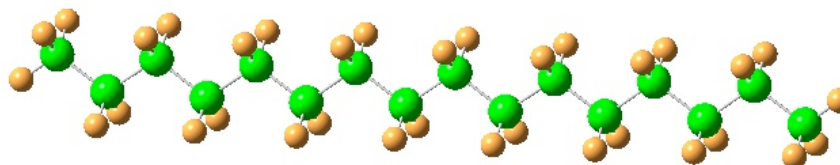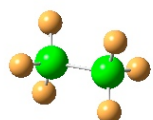
Objectives

❑ Implement a computational tool to determine the binary mass diffusion coefficients of hydrocarbon from **fully atomistic Molecular Dynamics simulations**

❑ Identify the effect of molecular structure on diffusivity
Possible factors that can be used to take into account morphology

❑ The validated computational tool can be used to gain insights on the transport properties of various systems at different temperatures where experimental data are not available

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Computational approach

1. <u>Fully atomistic</u> force field parameters (OPLS-AA)

2. Canonical ensemble (NVT ensemble)

   : remove the pressure coupling effects

3. Systems of ~7000 molecules, 500 – 1000K, 1 atm

5. 1.0 *fs* time step for numerical integration

7. 7 *ns* relaxation time for the integral of correlation functions
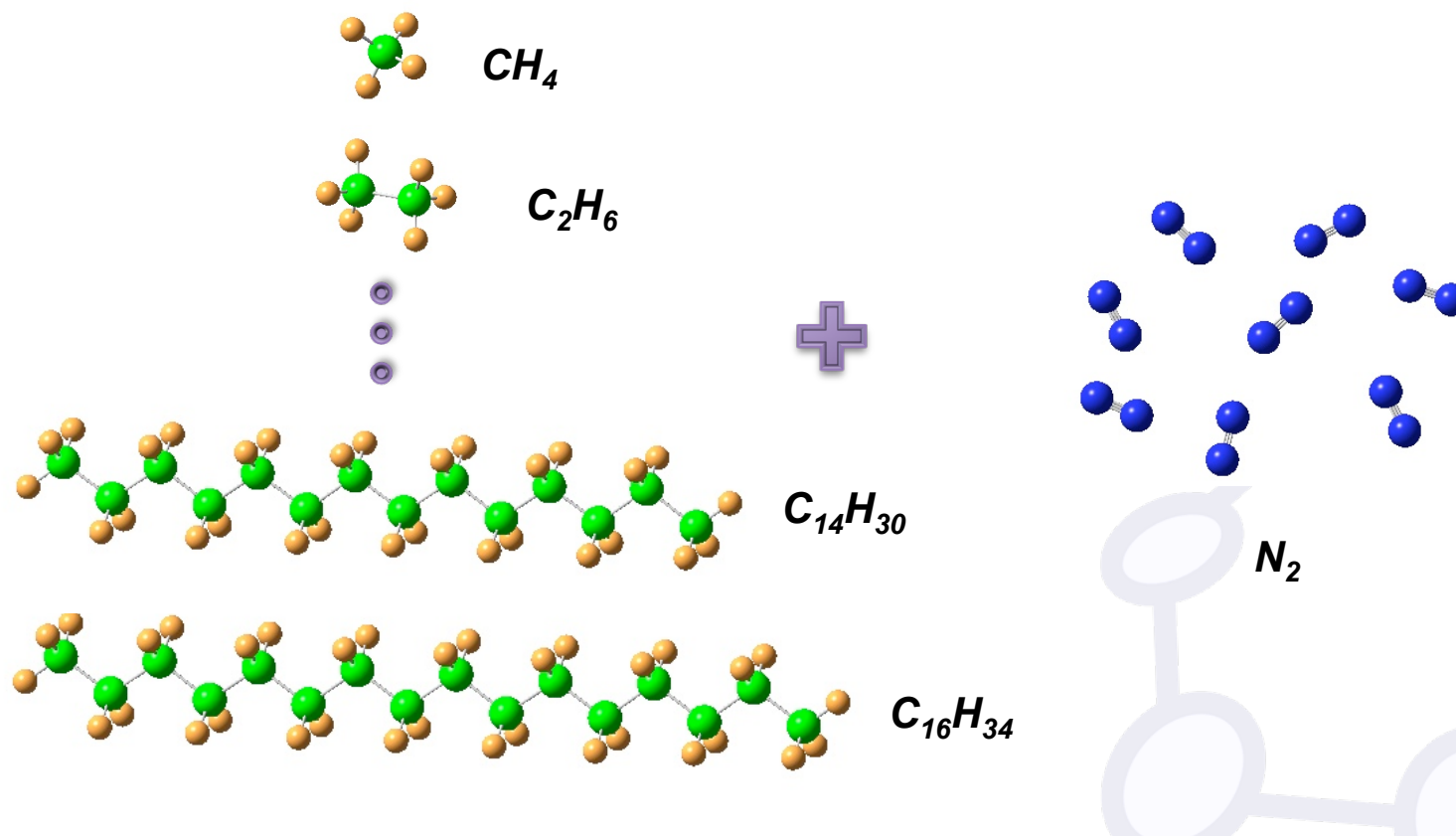
Benchmark of the computational approach
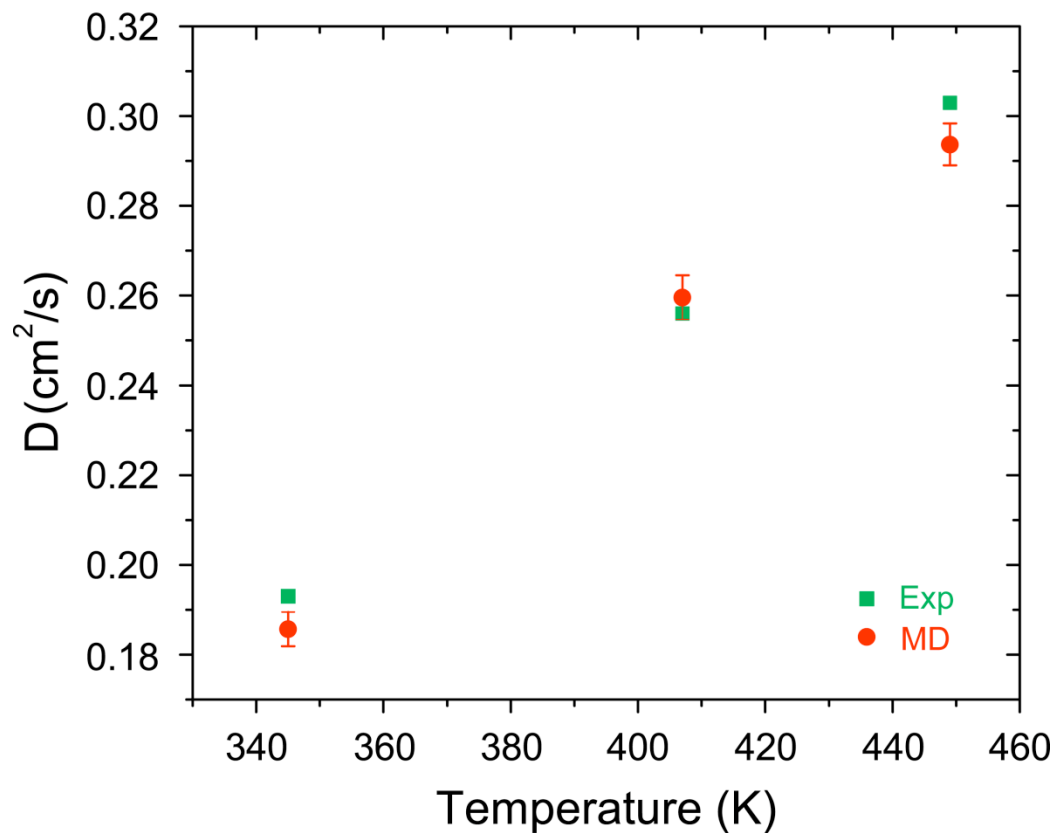
Mixture	T [K]	D_{12} [cm^2/s] Exp	MD
C_2H_6/N_2	345	0.193	0.186
	407	0.256	0.259
	449	0.303	0.294
C_5H_{12}/N_2	353	0.136	0.121

[Exp:

D. Gavril, J. Chromatography A,

1037, Vol. 147, 2004]

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Target systems -1

N-alkanes/N_2 mixtures (300 alkanes + 3000 N_2)

CH_4

C_2H_6

$C_{14}H_{30}$

$C_{16}H_{34}$

N_2

Comparison with C-E equation [n-alkanes]

Average relative deviation [%]
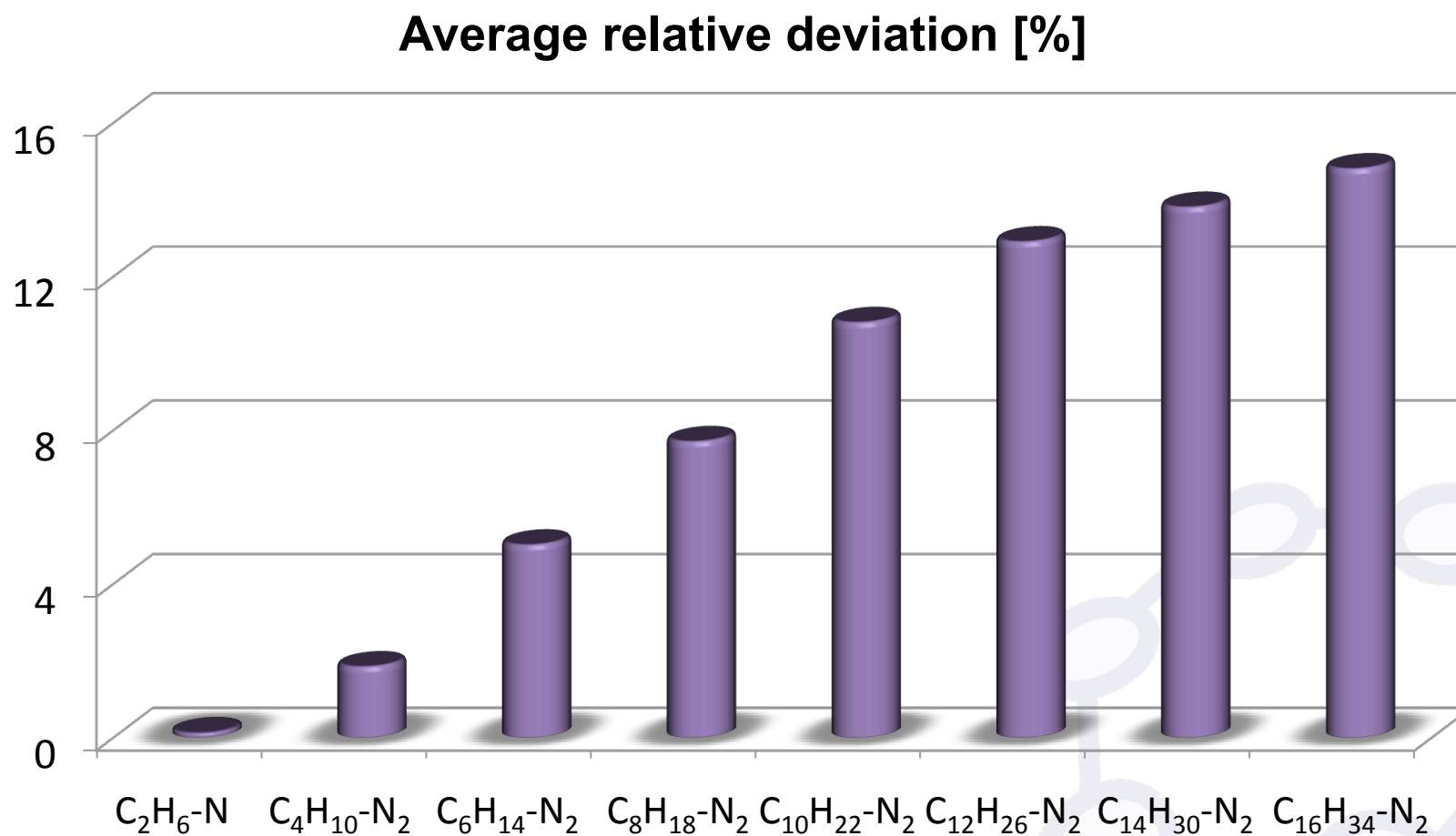
Target systems -2

Cycloalkanes/N_2 mixtures (300 alkanes + 3000 N_2)

C_6H_{12}

$C_{10}H_{20}$

$C_{14}H_{24}$

$+$

N_2

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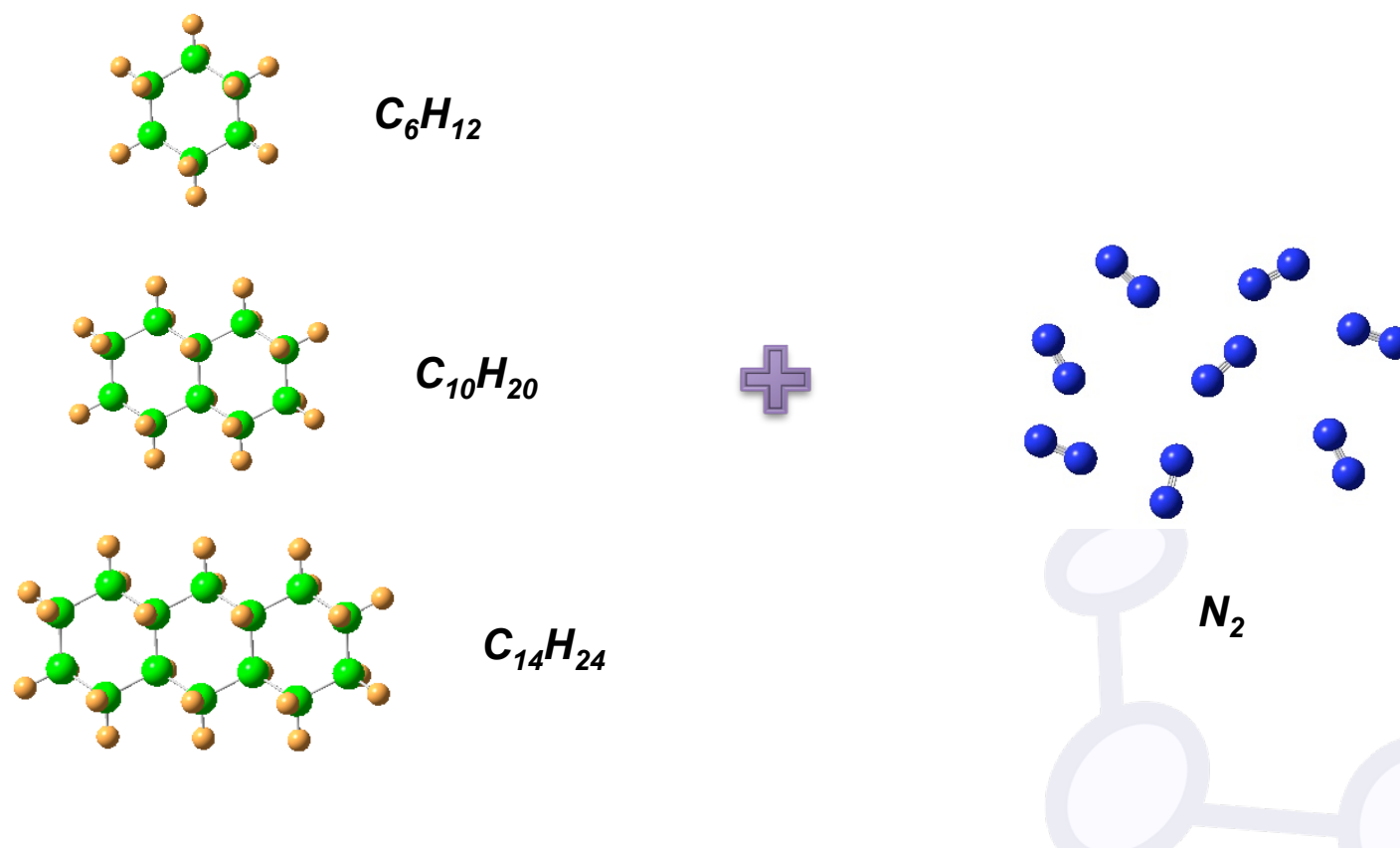
Comparison with C-E equation [cycloalkanes]

Average relative deviation [%]

C$_6$H$_{12}$-N$_2$ C$_{10}$H$_{18}$-N$_2$ C$_{14}$H$_{24}$-N$_2$

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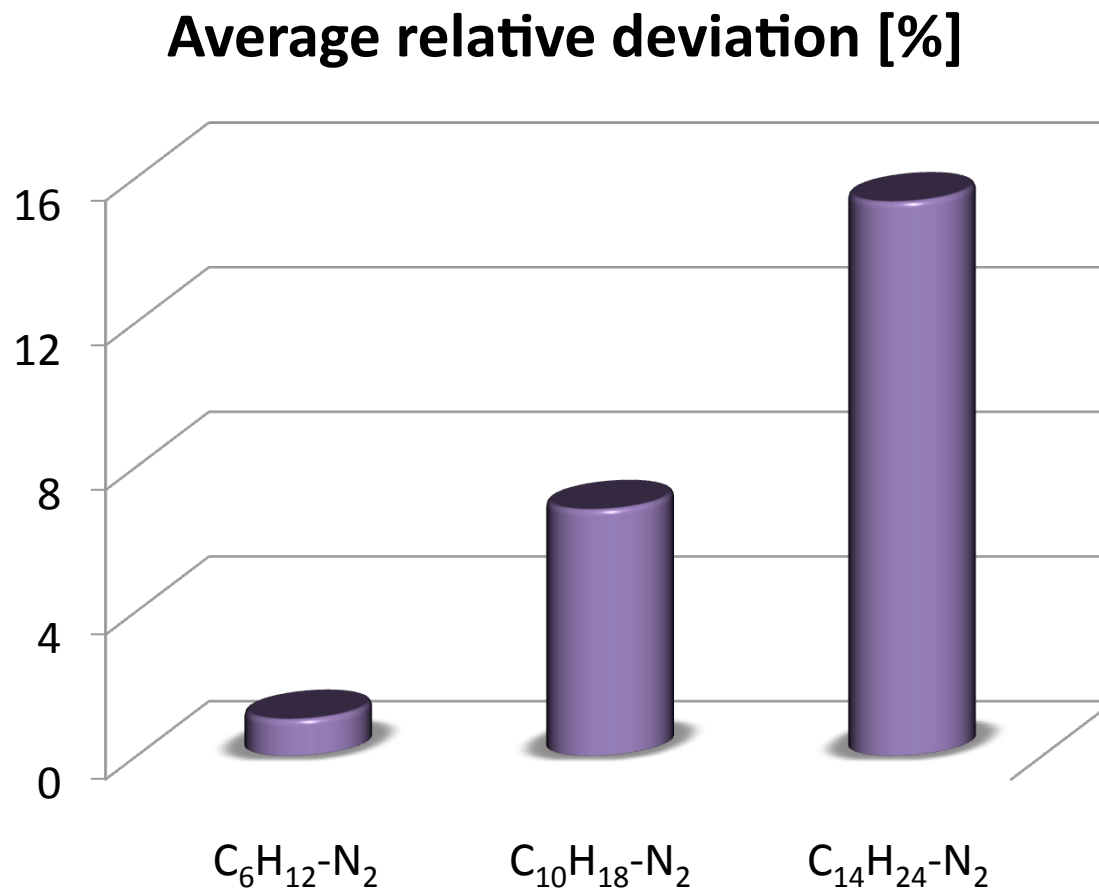
Milestones

- Transport properties of hydrocarbons using MD simulations (emphasis on compounds present in the JetSurF mechanism)

- N-alkanes and branched alkanes

- Work in progress for cycloalkanes

- New L-J parameters that can be used in combustion codes

- Tracer coefficients for multi-component diffusion coefficients

Conclusions

❑ We have implemented a tool to compute binary mass diffusivities for hydrocarbons using atomistic simulations.

❑ This computational tool can be used to quantify the effect of molecular structure on diffusivity

❑ The combination of updated kinetics and transport data for jet fuel surrogates will allow the development of a kinetic mechanism that can be used in many combustion conditions, **including flames**.

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